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S.W. McElvany, J.H. Callahan, M.M. Ross, L.D. Lamb and D.R. Huffman

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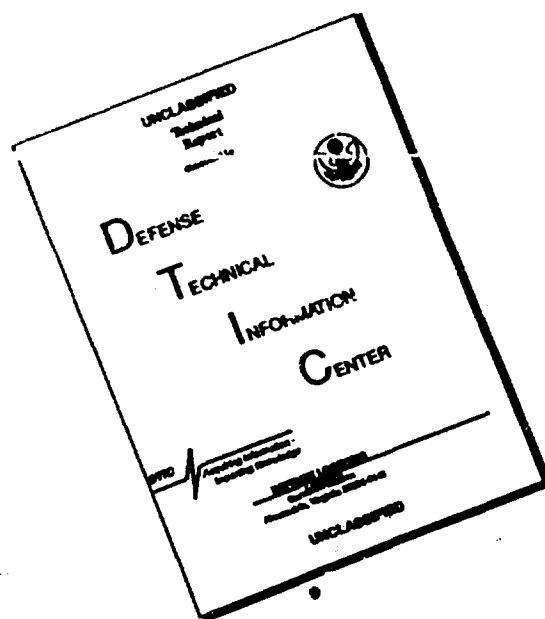| 14. SUBJECT TERMS			15. NUMBER OF PAGES
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by

Stephen W. McElvany, John H. Callahan, Mark M. Ross
Lowell D. Lamb and Donald R. Huffman

Code 6113 / Chemistry Division
Naval Research Laboratory
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Large Odd-Numbered Carbon Clusters from Fullerene-Ozone Reactions

Stephen W. McElvany, John H. Callahan, Mark M. Ross, Lowell D. Lamb, Donald R. Huffman

The odd-numbered carbon clusters C_{119}, C_{129}, and C_{139} have been observed in the mass spectra of toluene extracts of fullerene soots and of the products of ozone-fullerene reactions. Specifically, ozone-C_{60} reactions yield C_{119}, ozone-C_{70} reactions yield C_{139}, and ozone-(C_{60}/C_{70}) reactions produce C_{119}, C_{129}, and C_{139}. These unexpected species correspond to dimers of C_{60}, C_{60}/C_{70}, and C_{70}, respectively, less one carbon atom, and are stable gas-phase ions with behavior similar to that of fullerenes. The results suggest a new route to functionalization and derivatization of fullerenes through controlled ozone-catalyzed cage-opening reactions.

Numerous studies have shown that there is a wide variety of fullerene chemical reactions (1). For example, one unusual aspect of fullerenes is their ability to undergo coalescence reactions that result in larger fullerenes (2–4). Although the details of these reactions vary, in all cases observed to date coalescence apparently was caused by photon-induced radiation damage of fullerenes, and in all cases the reaction products had even numbers of carbon atoms.

In a recent mass-spectral investigation of large fullerenes, we detected the presence of the odd-numbered, pure carbon clusters C_{119}, C_{129}, and C_{139} in toluene extracts of several fullerene soot samples, which we speculated to be the products of coalescence of two C_{60}'s, a C_{60} and C_{70} and two C_{70}'s, respectively. These large, odd-numbered carbon clusters are unexpected, given the overwhelming evidence for the preferential stability of large, even-numbered carbon clusters (5). Results from a subsequent series of ozonolysis experiments support this interpretation and suggest that oxidation plays a key role in the production of these unusual species. These results have implications for several important issues in fullerene chemistry, including chemical reaction mechanisms and the resulting fullerene-based products, coalescence of fullerenes, and the molecular structure consideration raised by the existence of odd-numbered "fullerenes."

A typical thermal desorption–negative ion mass spectrum (6, 7) of a toluene extract (8) of a commercial soot sample (9) is shown in Fig. 1. Although not shown, C_{60}^- and C_{70}^- are approximately 10^3 to 10^4 times more abundant than the base peak in this spectrum. As expected, the abundances of fullerene ions (C_n^-, $n > 74$) generally decrease with increasing size, with anomalously abundant C_{84} and C_{90}. However, in addition to the even-numbered carbon clusters, ions are observed corresponding to C_{119}, C_{129}, and C_{139}. These odd-numbered carbon clusters were detected in a commercially available, unchromatographed mixture of fullerenes (9), as well as in toluene extracts of various fullerene soots [Polygon, SES (9), and "homemade" soot (7) produced at the Naval Research Laboratory].

In order to test the interpretation of the mass-spectral results, two alternative explanations had to be ruled out. Namely, it was possible that these clusters were not stable species but only artifacts of the mass spectrometry, that is, these ions were generated in the desorption-ionization process. In contrast to positive ion or laser desorption analysis, which may be complicated by fragmentation or coalescence of molecular species, previous studies of fullerenes indicate that thermal desorption–negative ion analysis is much less prone to these artifacts (7). A second possibility was that these were not pure carbon molecules. The relative ion abundances in the distribution from mass-to-change (m/z) ratios 1428 to 1433 were measured to be identical (within experimental error) to those calculated for C_{119} based on the natural ^{13}C abundance (see inset of Fig. 1). Similar results were obtained for C_{129} which indicated that these ions correspond to odd-numbered all-carbon species. (The abundance of C_{139}, however, was too low to allow this type of analysis.) Further investigations showed that the presence of the odd-numbered carbon clusters is not affected by the solvent, as they are also observed in hexane and benzene extracts of fullerene-rich soot. Careful inspection of mass spectra (not shown) of the raw (unextracted) soot revealed very low abundances of these ions (~500 times less abundant than neighboring even-n C_n). This observation and the analysis of the soot toluene extract (Fig. 1) suggest that the odd-numbered clusters are more soluble than the comparably sized even-numbered fullerenes. In addition, the use of ammonia or argon instead of methane as the buffer gas in the analysis yielded similar results, indicating that the formation of odd-numbered clusters is not due to the buffer gas.

As a complement to the negative ion analyses described above, electron ionization to generate positive ions of thermally
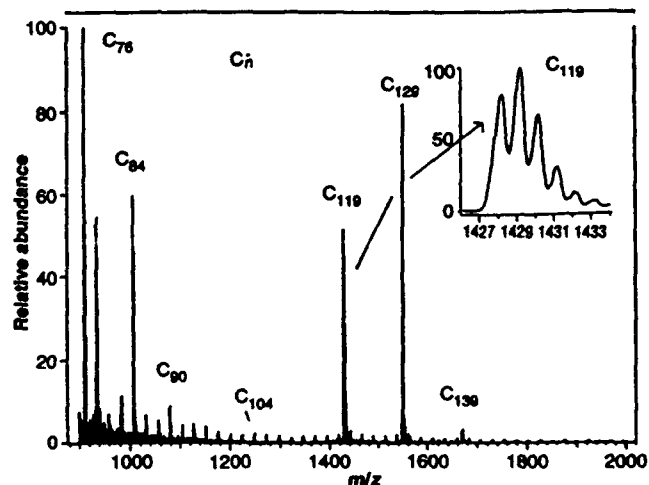

Fig. 1. Negative ion mass spectrum of a toluene extract of graphitic soot with the inset showing the expanded region around C_{119}^-.

S. W. McElvany, J. H. Callahan, M. M. Ross, Code 6113/Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5320.
L. D. Lamb and D. R. Huffman, Department of Physics, University of Arizona, Tucson, AZ 85721.

desorbed species was also used to rule out possible artifacts due to the ionization method. A comparison of negative ion and positive ion spectra of a toluene extract, showing a narrow mass range between m/z 1350 and 1600, is shown in Fig. 2. As expected, whereas the negative ion mass spectrum shows almost exclusively C_{119}^- and C_{129}^- in this range, the positive ion mass spectrum shows extensive fragmentation. Specifically, lower mass ions corresponding to C loss (C_{118}^+ and C_{128}^+) and subsequent C_2 losses (C_{116}^+ and C_{114}^+ and C_{126}^+, and C_{124}^+) from C_{119}^+ and C_{129}^+, respectively, were observed. Attempts to confirm these fragmentations with tandem mass spectrometry methods were unsuccessful, indicating that these species are relatively stable gas-phase ions. For example, no fragment ions could be observed from collision-induced dissociation (CID) of C_{119}^+ or C_{119}^- with xenon collision gas and a collision energy of 200 eV (laboratory frame; ~17 eV center-of-mass).

In an attempt to detect these species with different ionization methods and mass spectrometers, CO_2 laser desorption on a Fourier transform mass spectrometer (FTMS) was used. When this proved unsuccessful, a wire emitter probe similar to that used with the quadrupole instrument in the above studies was constructed for use with the FTMS. Negative ions of C_{119} and C_{129} were observed when thermal electron attachment was used, in addition to the usual fullerene ions. Secondary ion mass spectrometry showed neither positive nor negative ions of the odd-numbered carbon clusters from these samples.

It is logical to conclude that C_{119}, C_{129}, and C_{139} correspond to "dimers" of C_{60}, C_{60}/C_{70}, and C_{70} less one carbon atom, respectively. Although loss of a carbon atom in a reaction of two fullerenes

is thermodynamically "expensive," if oxygen were involved, the thermodynamically favorable loss of CO or CO_2 could drive this reaction. We investigated this possibility by bubbling ozone through toluene solutions of pure C_{60}, pure C_{70}, and a 1/1 mixture (by weight) of pure C_{60} and pure C_{70} in toluene for up to 20 hours (10). Figure 3 shows results of negative ion analysis of the three solutions, each exposed to ozone for 1 hour. (There were no visible changes observed in the solutions following ozone exposure.) The mass spectrum in Fig. 3A shows that the ozone-C_{60} reaction yields predominately C_{119}, in addition to lower abundances of C_{118}, C_{116}, and C_{114}. Figure 3B shows that the ozone-C_{70} reaction yields C_{139} and lower abundances of C_{138}, C_{136}, and C_{134}. The reaction of the C_{60}/C_{70} mixture with ozone yields all of the above products ions in addition to the most abundant product corresponding to C_{129}, with lower abundances of C_{128}, C_{126}, and C_{124} (Fig. 3C). In these solutions prior to ozone exposure, the odd-numbered carbon cluster ions either were not detected or were at least 100 times less abundant than in the ozone-exposed samples. The relative abundance of the odd-numbered clusters in solution following ozone exposure is similar to that described in the soot extracts in Fig. 1 (0.01 to 0.1% of C_{60}). These preliminary studies indicated that ozone exposures longer than 1 hour result in either no increase in reaction products or an overall decrease in all species. It is important to note in Fig. 3C that the greater abundance of C_{119} relative to that of C_{139} indicates a greater reactivity of C_{60} than C_{70}. This result is consistent with a recent report that fullerenes in solution are oxidized readily upon exposure to ozone, with C_{60} showing a greater reactivity than C_{70} (11).

The ozone exposure study strongly indicates that these species are products of fullerene-ozone reactions and not products of the desorption-ionization process. In a further test of this hypothesis, we were able to form C_{119} also by exposure of a toluene solution of C_{60} and benzil to ultraviolet radiation (12), a procedure that has been used to generate large quantities of $C_{60}O$ (13). It should be noted, however, that the graphite arc fullerene production process can also yield these odd-numbered carbon clusters. In this case, we do not know if oxygen is involved in the production of these species. The reason why these species have not been observed previously may be that laser desorption mass spectrometry is most often used to analyze soot extracts. This is consistent with our unsuccessful CO_2 laser desorption analyses and suggests that these species are unstable under laser-induced desorption-ionization conditions.

This study has shown that certain size, odd-numbered, all-carbon species can be formed by reaction of fullerenes with ozone, and in some cases during fullerene soot production. It is interesting to note that in previous studies of fullerene coalescence reactions, only even-numbered carbon cluster were observed (3–5). The laser-induced coalescence of C_{60} in vacuum, for example, yielded a distribution of even-numbered carbon clusters centered approximately on C_{118}, which are thought to result from multiple C_{60} reactions in which small even-numbered carbon fragments can be gained or lost. These studies suggest that these even-numbered coalescence products are similar in structure to fullerenes because of the measured stability with respect to collisions (3) and oxidative ion-molecule reactions (4). In this study, C_{119}, C_{129}, and C_{139} nominally correspond to the combinations of C_{60} +
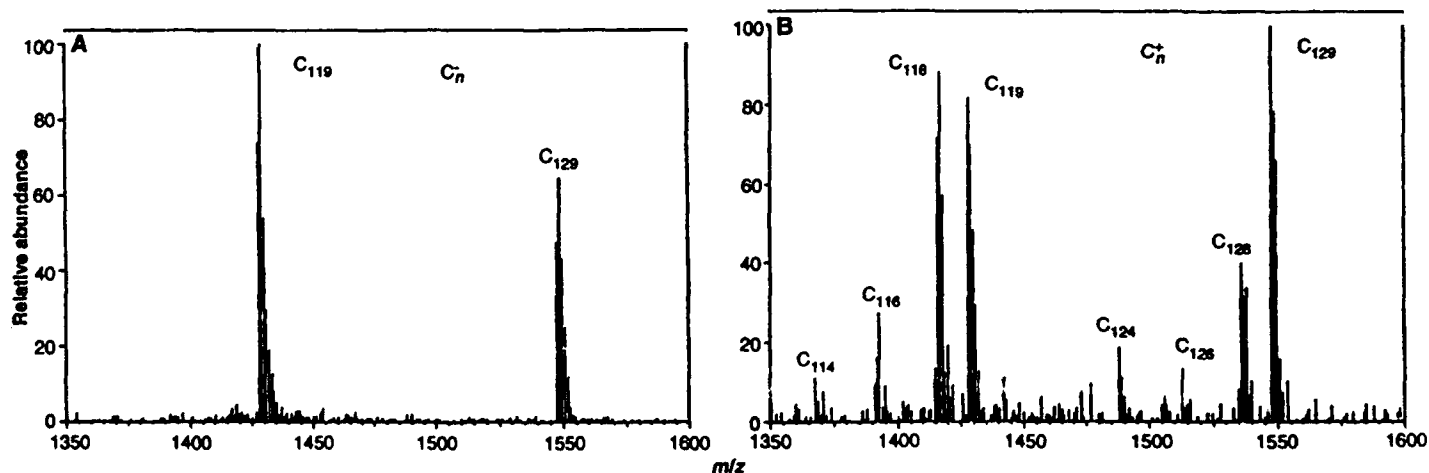

Fig. 2. Comparison of a negative ion mass spectrum (A) of toluene extract showing little or no fragmentation and a positive ion electron ionization mass spectrum (B) that contains significant fragmentation corresponding to loss of C followed by C_2 units.

C_{59}, C_{60} + C_{69} or C_{70} + C_{59}, and C_{70} + C_{69}, respectively. The stability toward CID and the C_2-loss fragmentation (following an initial C loss to yield an even-numbered species) from the positive ions are indicative of fullerene-like structures. However, the structures of these unexpected products are unknown.

Although it might be thermodynamically reasonable for an oxidative reaction of two C_{60} molecules to yield C_{119} (C_{60} + C_{59}) and CO_2, it is not clear how C_{60} and C_{59} might bond together. Although we were not able to determine the structures of C_{119}, C_{129}, and C_{139} in this work, our results offer strong evidence that they originate from the smaller fullerenes C_{60} and C_{70} and thus several configurations can be postulated. One possible scheme for attaching C_{59} to C_{60} would join the three nearest neighbors of the "missing" carbon atom in the C_{59} to three

atoms (1, 3, and 5) of a hexagonal ring on the C_{60} with sp^3 bonds. Alternatively, large-scale rearrangements may occur following the initial reaction, and, for example, the resultant C_{119} (and C_{118}, C_{116}, and so forth) may not resemble two bound C_{60}'s but a large, single coalescence product. Such extensive rearrangements can be favorable, as evidenced by the coalescence of large monocyclic carbon species (C_{18}, C_{24}, and C_{30}) to yield fullerenes (14).

The results of this study indicate that ozone exposure of C_{60} and C_{70} can cause an opening of the fullerene cage and a subsequent reaction with another C_{60} or C_{70} to yield a larger carbon cluster. This result seems to be consistent with the observations that the opening of fullerene nanotubes requires oxidative conditions (15), whereas photo-induced polymerization of C_{60}, in which the balls are linked,

does not occur in the presence of air (16). In addition, other fullerene coalescence and irradiation studies may not have yielded these odd-numbered clusters because of the lack of oxygen (or ozone) or these products were not observed due to the use of desorption-ionization methods. In any case, this work suggests a new area of fullerene chemistry through ozone-catalyzed reactions. A broad range of fullerene derivatization reactions may be envisioned in which controlled cage opening followed by functionalization, substitution, or encapsulation might be possible.

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8. Soot samples were extracted by using either a Soxhlet apparatus, sonication, or simply by letting a soot-solvent mixture stand for several hours, followed by filtration.
9. An unchromatographed toluene extract of fullerene soot was obtained from Polygon Enterprises, Inc., Waco, TX, and raw, unextracted fullerene soot was obtained from Polygon and SES Research Corp., Houston, TX.
10. Solutions of pure C_{60} (99 + %), pure C_{70} (99 + %), and a 1:1 mixture of pure C_{60} and pure C_{70} were prepared as 2, 1, and 1 mg/ml in toluene, respectively, for ozone exposure studies. Ozone was produced by passing oxygen through an ultraviolet lamp ozone generator and bubbled through the fullerene solutions at room temperature at a rate of ~200 ml/min (100 ppm O_3 in O_2) for up to 20 hours. Aliquots (1 ml) were removed periodically for analysis.
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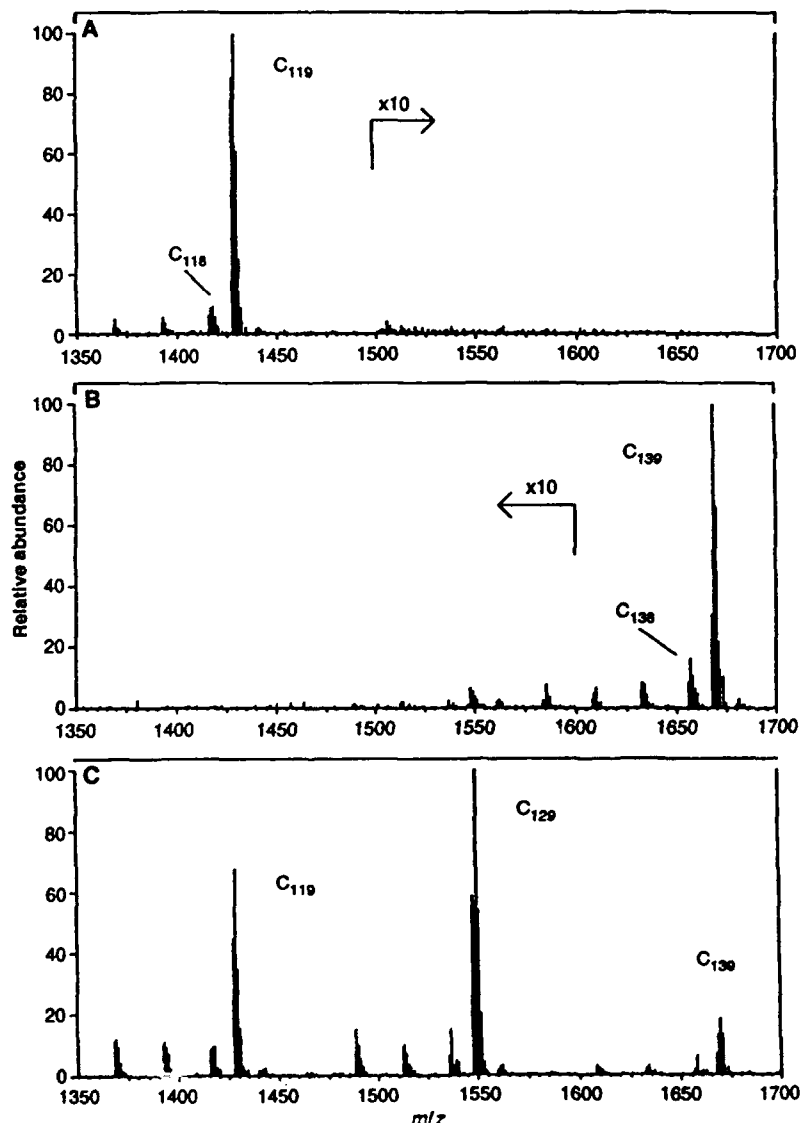
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Fig. 3. Negative ion mass spectra of 1-hour ozone-exposed solutions containing (**A**) pure C_{60}, (**B**) pure C_{70}, and (**C**) a 1/1 C_{60}/C_{70} mixture showing C_{119}, C_{139} and C_{119}, C_{129} and C_{139}, respectively.

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